

CHROMIUM AND COMPOUNDS

HEXAVALENT CHROMIUM

Hexavalent Chromium was identified as a toxic air contaminant under California's air toxics program (AB 1807) in 1986.

Chromium compounds are federal hazardous air pollutants and were identified as toxic air contaminants in April 1993 under AB 2728.

CAS Registry Number: Chromium = 7440-47-3
Chromium VI = 18540-29-9

Cr

Molecular Formula: Chromium: Cr
Chromium VI: Cr^{+6}

Chromium is an odorless, steel-gray, hard metal that is lustrous and takes a high polish. It is extremely resistant to corrosive agents. Chromium can exist in water in several different states but under strongly oxidizing conditions, may be converted to the hexavalent state and occurs as chromate anions. Chromium is soluble in dilute hydrochloric acid and sulfuric acid but not nitric and strong alkalies and alkali carbonates (Merck, 1989).

Chromium metal is not found in nature, but is produced principally from the mineral chromite (chrome ore). Chromite contains chromium in the +3 oxidation state, or chromium (III). Chromium combines with various other elements to produce compounds, the most common of which contain either chromium (III), which is trivalent (the +3 oxidation state) or chromium (VI), which is hexavalent chromium (the +6 oxidation state) (ARB, 1986d). Chromium (III) compounds are sparingly soluble in water, while most chromium (VI) compounds are readily soluble in water (U.S. EPA, 1994a). Chromium forms a number of compounds in other oxidation states, however, those of +2 (chromous), +3 (chromic) and +6 (chromates) are the most important (HSDB, 1995).

Thousands of chromium (III) compounds exist, exhibiting a wide range of colors, structures, and chemical properties. Chromium (VI) compounds are produced industrially by heating chromium (III) compounds in the presence of mineral bases (such as soda ash) and atmospheric oxygen. Most chromium (VI) solutions are powerful oxidizing agents under acidic conditions, but much less oxidizing under basic conditions. Depending on the concentration and acidity, chromium (VI) can exist as either chromate ion (CrO_4^{-2}), or as dichromate ion ($\text{Cr}_2\text{O}_7^{-2}$) (ARB, 1986d).

Chromium (III) is the most stable oxidation state, forming coordination complexes which are exclusively octahedral, with ligands such as water, urea, sulfates, ammonia, and organic acids. Stable complexes can thus be formed with anions, acids, peptides, proteins, nucleic acids, and other macromolecules.

Chromium (VI) is virtually always bound to oxygen in ions such as chromates (CrO_4^{-2}) and dichromates ($\text{Cr}_2\text{O}_7^{-2}$). Chromium (VI) ions are strong oxidizing agents and are readily reduced to chromium (III) in acid or by organic matter.

Physical Properties of Chromium

(For physical properties of some chromium compounds see Table I.)

Synonyms: chrom

Atomic Weight:	51.966
Atomic Number:	24
Valences:	1 - 6
Boiling Point:	2642 °C
Melting Point:	1900 °C
Density/Specific Gravity:	7.14
Vapor Pressure:	1 mm Hg at 1616 °C

(HSDB, 1995; Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

Chromium occurs naturally as a trace component of most crude oils, and the concentrations of chromium found in residual and distillate oils have been measured. Available information suggests that the chromium is emitted in the trivalent state from oil combustion, sewer sludge incineration, cement production, municipal waste incinerators, and refractories (ARB, 1986d). Chromium is used for corrosion resistance, steel production, and as protective coating for automotive and equipment accessories. It is a permanent and stable inorganic pigment used for paints, rubber, and plastic products (Howard, 1990). Chromium has also been detected but not quantified in motor vehicle exhaust by the Air Resources Board (ARB) (ARB, 1995c).

Chrome plating is a source of chromium (VI) emissions in the state. Chrome electroplating operations are conducted in baths containing chromic acid and during the plating process, bubbles of gas are emitted through the surface of the bath. These bubbles carry entrained chromium (VI) into the air. Chromium emissions can occur from chromium (VI) firebrick lining of glass furnaces (ARB, 1986d). Although it is a minor source of emissions, the most commonly seen hexavalent chromium is lead chromate. Lead chromate is the pigment in the yellow paint used to mark traffic lanes. In addition, hexavalent chromium in water solution is converted through electroplating (decorative chrome plating) to the bright metallic chromium coating seen on plastic or metal

products such as shower heads or car bumpers. Although not commonly seen by the general public, one of the most important uses of chrome plating is to apply a hard, smooth surface to machine parts such as crankshafts and printing rollers. This process is known as "hard" chrome plating. Chromic acid anodizing is another industrial metal finishing process which uses hexavalent chromium.

The primary stationary sources that have reported emissions of chromium compounds in California are lumber and wood products manufacturers, stone, clay, and glass production, and petroleum refining. Reported emissions of chromium (VI) from stationary sources in California are electrical services, aircraft and parts manufacturing, and steam and air conditioning supply services (ARB, 1997b).

Chromic acid is registered as a fungicide and insecticide. It is used for wood and lumber protection treatments. It may also be used to treat lumber used for pilings for the control of aquatic organisms. Sodium dichromate is registered as an insecticide. It is used as a wood preservative to prevent termite damage to wood products (DPR, 1996).

The licensing and regulation of pesticides for sale and use in California are the responsibility of the Department of Pesticide Regulation (DPR). Information presented in this fact sheet regarding the permitted pesticidal uses of chromic acid and sodium dichromate has been collected from pesticide labels registered for use in California and from DPR's pesticide databases. This information reflects pesticide use and permitted uses in California as of October 15, 1996. For further information regarding the pesticidal uses of these compounds, please contact the Pesticide Registration Branch of DPR (DPR, 1996).

B. Emissions

The total emissions of chromium (VI) and chromium compounds from stationary sources in California are estimated to be at least 6,400 and 9,000 pounds per year, respectively, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b).

The ARB adopted an airborne toxic control measure in 1988 to control emissions of chromium (VI) from chrome plating and chromic acid anodizing operations. The control measure contains both an interim requirement (95 percent control) and a technology forcing requirement (99.8 percent control) (ARB, 1989d).

In the past, compounds containing chromium (VI) such as sodium dichromate or lead chromate were added to cooling tower water to control corrosion in the towers and associated heat exchangers. The ARB adopted in 1989 a statewide airborne toxic control measure which prohibits the use of hexavalent chromium in cooling towers (ARB, 1989e).

C. Natural Occurrence

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases (U.S. EPA, 1994a). Chromium (III) is a component of most soils. In areas of serpentine and peridotite rocks, chromite is the predominant chromium mineral. Deposits of 5 to 10 percent chromite have been found in beach sands and stream placers in several California counties. Also, chromium has been found in non-serpentine areas in the state at concentrations as high as 500 parts per million (ARB, 1986d).

Soil chromium is generally in an insoluble, biologically unavailable form, mainly as the weathered form of the parent chromite or as the chromium (III) oxide hydrate. Weathering and wind action can transport soil chromium to the atmosphere; generally, such mechanical weathering processes generate particles greater than 10 micrometers in diameter, which have significant settling velocities. The extent to which natural sources of chromium contribute to measured ambient chromium levels in California is not known. Ambient chromium derived from soil is expected to exist as chromium (III) (ARB, 1986d).

AMBIENT CONCENTRATIONS

Chromium compounds and chromium (VI) are routinely monitored at the statewide ARB toxics network. When chromium was formally identified as a toxic air contaminant, the ARB estimated a population-weighted annual concentration of 8.9 to 17.8 nanograms per cubic meter (ng/m^3) (ARB, 1986d). The network's mean concentration of chromium compounds from January 1996 through December 1996 is estimated to be $3.9 \text{ ng}/\text{m}^3$. The network's mean concentration of chromium (VI) from January 1996 through December 1996 is estimated to be $0.13 \text{ ng}/\text{m}^3$ (ARB, 1997c). Data on ambient concentrations of hexavalent chromium indicate that hexavalent chromium comprises 3 to 8 percent of ambient total chromium. Chromium in ambient air has been reported to contain principally respirable particulates, with a mass median diameter of about 1.5 to 1.9 micrometers (ARB, 1986d).

INDOOR SOURCES AND CONCENTRATIONS

The extent of exposure to airborne chromium in the indoor environment, other than in the workplace, is not known. There are no direct consumer uses of chromium which could lead to emission of chromium compounds. Although cigarettes are known to contain chromium, the intake of chromium from smoking is not known (ARB, 1986d).

In a field study conducted in southern California, investigators collected particles (PM_{10}) inside 178 homes and analyzed the particle samples for selected elements, including chromium. Two consecutive 12-hour samples were collected inside and immediately outside each home.

Chromium was present in measurable amounts in less than 25 percent of the indoor or outdoor samples (Pellizzari et al., 1992).

A southern California study measured chromium inside vehicles during the summer of 1987 and winter of 1988. An average chromium concentration of 12 ng/m³ and a maximum concentration of 41 ng/m³ were measured (Shikiya et al., 1989).

ATMOSPHERIC PERSISTENCE

Atmospheric reactions of chromium compounds were characterized in field reaction studies and laboratory chamber tests. These results demonstrated an average experimental half life of 13 hours (RTI, 1988).

Physical removal of chromium from the atmosphere occurs both by atmospheric fallout (dry deposition) and by washout and rainout (wet deposition). Measurements have shown that most chromium deposition occurs through wet deposition. Chromium particles of less than 5 micrometers (aerodynamic equivalent) diameter may remain airborne for extended periods of time, allowing long distance transport by wind currents. Because of this, meteorological conditions can play a significant role in the dispersion of chromium emitted from some sources (ARB, 1986d).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics “Hot Spots” Program (AB 2588). Of the risk assessments reviewed as of April 1996, chromium (VI) was the major contributor to the overall cancer risk in 113 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 131 of these risk assessments. Chromium (VI) also was the major contributor to the overall cancer risk in 43 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million, and contributed to the total cancer risk in 87 of these risk assessments (OEHHA, 1996a).

Chromium and chromium compounds were the major contributors to the overall cancer risk in 1 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 6 of these risk assessments. Chromium and chromium compounds also were the major contributors to the overall cancer risk in 1 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million, and contributed to the total cancer risk in 3 of these risk assessments (OEHHA, 1996a).

For non-cancer health effects, chromium (VI) contributed to the total hazard index in 37 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1, and presented an individual hazard index greater than 1 in 9 of these risk assessments (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to chromium and chromium compounds are by ingestion and inhalation (U.S. EPA, 1994a).

Non-Cancer: The trivalent and hexavalent forms are believed to be the biologically active species, but their health impacts are not identical, in part because chromium (VI) readily penetrates biological membranes while chromium (III) generally does not. Chromium (III) is an essential trace element and a daily intake of 50 to 200 micrograms per day is recommended for normal glucose, protein, and fat metabolism. The body can reduce chromium (VI) to chromium (III) and this detoxification leads to increased levels of chromium (III) (U.S. EPA, 1994a). The principal acute effects of chromium (VI) exposure are renal toxicity, gastrointestinal hemorrhage, and intravascular hemolysis. In occupational settings the most commonly reported chronic effects of chromium exposure include contact dermatitis, skin ulcers, irritation and ulceration of the nasal mucosa and perforation of the nasal septum. Less common are reports of hepatic and renal damage and pulmonary effects (bronchitis, asthma, and bronchospasm) (NIOSH, 1975).

A chronic non-cancer Reference Exposure Level (REL) of 2.0×10^{-3} micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) is listed for hexavalent chromium in the California Air Pollution Control Officers Association Air Toxics "Hot Spots" Program, Revised 1992 Risk Assessment Guidelines. The toxicological targets considered for chronic toxicity are the respiratory tract, kidney, gastrointestinal system, and liver (CAPCOA, 1993).

Reference Concentrations (RfC) for chromium (III) and chromium (VI) are under review by the United States Environmental Protection Agency (U.S. EPA). The oral Reference Dose (RfD) for chromium (VI) is 0.005 milligrams per kilogram per day (mg/kg/d) and the RfD for chromium (III) is 1 mg/kg/d, based on no effects observed in rats exposed to chromium (III) in their diet (U.S. EPA, 1994a).

Limited human studies suggest that occupational chromium exposure may be associated with complications during pregnancy and childbirth. Inhalation studies in animals have not reported reproductive or developmental toxicity. Chromium (VI) has been reported to cause adverse developmental effects in orally exposed mice including decreased litter size, decreased fetal weight, and decreased fetal ossification. In males, testicular pathology has been reported with oral or injection exposure and dominant lethal effects have been reported with injection exposure (U.S. EPA, 1994a; ATSDR, 1993f).

Cancer: There is epidemiological evidence that exposure to inhaled chromium may result in lung cancer. These studies could not differentiate between chromium (VI) and chromium (III). The U.S. EPA has classified chromium (VI) in Group A: Human carcinogen with an estimated potency value of 1.2×10^{-2} (microgram per cubic meter)⁻¹. The U.S. EPA estimates that if an

individual were to breathe air containing chromium at $8 \times 10^{-5} \mu\text{g}/\text{m}^3$, over a lifetime, that person would theoretically have no more than a 1 in 1 million increased chance of developing cancer. The U.S. EPA classified chromium (III) in Group D: Not classifiable as to carcinogenicity in humans (U.S. EPA, 1994a). The International Agency for Research on Cancer has classified chromium (VI) in Group 1: Human carcinogen, and chromium (III) in Group 3: Not classifiable (IARC, 1990).

The State of California has determined under Proposition 65 that chromium (hexavalent compounds) is a carcinogen (CCR, 1996). The inhalation potency factor that has been used as a basis for regulatory action in California for chromium (VI) $0.15 (\text{microgram per cubic meter})^{-1}$ (OEHHA, 1994). In other words, the potential excess cancer risk for a person exposed over a lifetime to $1 \text{ ng}/\text{m}^3$ chromium is estimated to be no greater than 146 in 1 million. The oral potency factor that has been used as a basis for regulatory action in California for chromium (VI) is $4.2 \times 10^{-1} (\text{milligram per kilogram per day})^{-1}$ (OEHHA, 1994).

TABLE I - PROPERTIES OF CHROMIUM COMPOUNDS

Molecular Formula, Substance Name, & CAS Registry No.	Color	Molecular Weight	Density	Melting Point (°C)	Boiling Point (°C)
Ba•CrH ₂ O ₄ barium chromate CAS No: 10294-40-3	heavy yellow powder	255.36	4.49	---	---
Cl ₃ Cr chromic chloride CAS No: 10025-73-7	violet hexagonal crystals	158.38	1.76	1152	dissociates above 1300
CrF ₃ chromic fluoride CAS No: 7788-97-8	dark green needles	109.01	3.86	1000	sublimes at 1100
Cr ₂ O ₃ chromic oxide CAS No: 1308-38-9	green hexagonal crystals	152.02	5.2	~2435	~3000
Cl ₂ CrO ₂ chromium oxychloride CAS No: 14977-61-8	dark red fuming liquid	154.90	1.91	-96.5	115.7
CrBr ₂ chromous bromide CAS No: 10049-25-9	white, monoclinic crystals	211.84	4.36	842	---
CrCl ₂ chromous chloride CAS No: 10049-05-5	white, deliquescent crystals	122.92	2.88	824	---
CrF ₂ chromous fluoride CAS No: 10049-10-2	greenish, shiny crystals	90.01	3.80	894	---
CrO ₄ Pb lead chromate CAS No: 7758-97-6	orange-yellow powder	323.19	6.3	844	decomposes
Cr ₂ O ₇ •Na ₂ sodium dichromate CAS No: 10588-01-9	red to orange monoclinic crystals	261.98	2.35	356.7	---

(ARB, 1985; Sax, 1989; Merck, 1989; Sax, 1987)